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Effect of Ni/Fe ratio on the performance and stability of the Fe-air rechargeable battery using a $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ electrolyte

Atsushi Inoishi ^{a,*}, Takaaki Sakai ^{a,b}, Young-Wan Ju ^c, Shintaro Ida ^{a,d},
Tatsumi Ishihara ^{a,d}

^a Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan

^b Center for Molecular Systems, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan

^c School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan, 689-798, Republic of Korea

^d International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan

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ABSTRACT

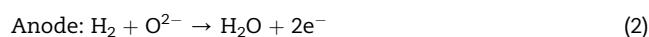
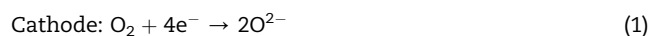
The effect of the Ni/Fe ratio in the anode composition of Fe-air rechargeable battery using LaGaO_3 -based oxide ion conducting electrolyte was studied in terms of the discharge performance, including discharge potential and stability of anode. A Pure Ni anode showed no potential plateau during discharge, and the cycle stability was significantly low. The highest stability and discharge potential was observed for a Ni–Fe (90:10). When the anode contained a large amount of Fe, such as those with ratio of Ni–Fe (30:70), the cycle stability was low due to the aggregation of particles with an increasing number of redox cycles.

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Introduction

Rechargeable battery with high energy density is strongly requested for averaging electricity [1]. Metal-air batteries are attracting significant interest as the next-generation of battery systems with extremely-high energy density [2–4]. Furthermore, solid state metal-air batteries are very interesting from the point of view of their reliability and stability. Recently, metal-air batteries using oxide ion conducting electrolytes have been reported [5–16]. In our previous work,

we reported that an Fe-air rechargeable battery using a LaGaO_3 -based oxide ion conducting electrolyte shows high performance, including discharge potential, and high capacity [5,7,8,11]. Since the Fe powder for redox couple is separated from the cell, the discharge of the proposed Fe-air battery proceeds according to the following electrode reactions:



* Corresponding author. Tel.: +81 92 802 2870; fax: +81 92 802 2871.

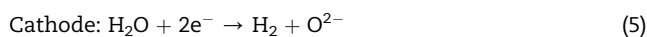
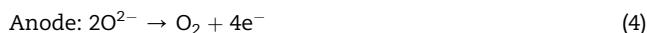
E-mail address: inoishi_a@cstf.kyushu-u.ac.jp (A. Inoishi).

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The Fe powder can react with H_2O generated in the cell to form H_2 , which can be used as the fuel for discharge. On the other hand, the electrochemical charge reaction proceeds according to the following electrode reactions:



During charging, the iron oxide is reduced by the H_2 generated by steam electrolysis, and oxygen is evolved to the air from air electrode. In our previous reports, we used Ni–Fe (90:10) and/or Ni–Fe (90:10)-based cermet electrodes as the anode. However, the effect of Ni/Fe ratio in the anode composition on the performance of the Fe-air rechargeable battery and stability for redox cycle is still not clear. Ju et al. reported that Ni–Fe (90:10) anode in solid oxide fuel cells is highly stable for redox cycle compared with pure Ni anode because addition of Fe into anode can protect from the deep reoxidation of anode [17]. Therefore, effect of addition of Fe into anode is highly important considering the redox stability, because anode in the Fe-air rechargeable battery is exposed to both the oxidation atmosphere and reducing atmosphere. Therefore, in this work, we studied the effect of Ni/Fe ratio of anode for discharge potential and cycle stability.

Experimental

An electrolyte-supported planar type single cell (17 mm in diameter and 0.3 mm thick) was consistently used in this study. $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LSGM) was prepared by a conventional solid state method using La_2O_3 (Kishida Chemical Co., Ltd., Japan), SrCO_3 (Rare Metallic Co., Ltd., Japan), Ga_2O_3 (Kojundo Chemical Laboratory Co., Ltd., Japan), and MgO (Wako Pure Chemical Industries, Ltd., Japan) as starting materials. The prepared mixed powder was calcined at 1273 K for 6 h, pressed into a disk, and then sintered at 1773 K for 6 h. The LSGM disk was polished to a thickness of 0.3 mm. Ni–Fe or Ni was used for the anode. Ni–Fe with different ratio (wt%) was synthesized by loading $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Kishida Chemical Co., Ltd., Japan) on NiO powder (Wako Pure Chemical Industries, Ltd., Japan) in aqueous solution. The obtained powder was calcined in air at 873 K to decompose the nitrate acid. For the pure Ni anode, commercial NiO powder was used with no further treatment. The $\text{Ba}_{0.6}\text{La}_{0.4}\text{CoO}_3$ (BLC) used for the cathode (air electrode) was prepared by a solid state reaction method using BaCO_3 (Rare Metallic Co., Ltd., Japan), La_2O_3 (Kishida Chemical Co., Ltd., Japan), Co_3O_4 (Kojundo Chemical Laboratory Co., Ltd., Japan). Ni or Ni–Fe powder for anode and BLC powder for cathode were painted on each face of the LSGM disk using a screen printing method with 5 mm diameter followed by calcination at 1373 K for 30 min. Weight of

electrode is ca. 2 mg. The Pt reference electrode was set close to the cathode using commercial Pt paste (Tanaka TR7908).

The prepared planer type single cell was set in an Al_2O_3 tube with molten Pyrex glass used as a gas sealant. 30 mg of Fe oxide powder was inserted under the cell without direct contact on the cell. Details of the experimental set-up are reported in our previous paper [5]. After heating the cell, humidified hydrogen (3 vol% H_2O) was fed into the Fe chamber to reduce the anode and Fe powder. After reduction, the gas composition of the Fe chamber was diluted with nitrogen (initial gas composition before discharge, 87.3% N_2 , 9.7% H_2 , and 3% H_2O) and then separated by two stop valves from the gas supply line to conduct the discharge measurement in a closed system. Pure oxygen was continuously supplied as oxidant with 100 mL/min of flow rate. The discharge capacity of the cell was measured by the four-probe method under a constant current of 10 mA/cm². Charging was performed by reduction with H_2 flow for 2 h after discharge. All of the electrochemical measurement was performed at 873 K. To calculate the discharge capacity, actual capacity (mAh) was divided by the amount of Fe powder inserted under the cell. Internal resistance was estimated with AC impedance analysis at 873 K. Impedance analysis was performed using a frequency response analyzer (Solartron, 1260) equipped with a potentiostat/galvanostat (Solartron, type 1270). The impedance spectra were measured in the frequency range from 0.1 to 10⁵ Hz with a signal amplitude of 10 mV at open circuit voltage. The electrode morphology and cross sectional image of the cell were observed using scanning electron microscopy (SEM; Keyence VE-7800).

Results and discussion

Before discussing the performance as an Fe-air battery with limited H_2 supply, which depends on H_2 formation rate from

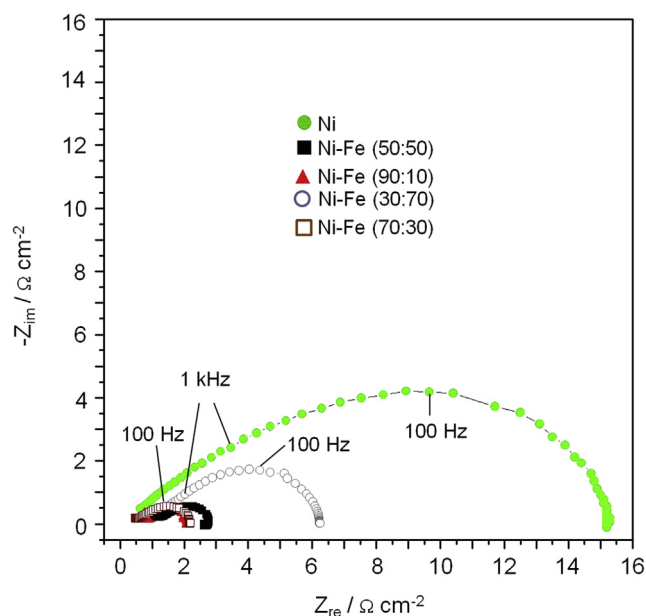


Fig. 1 – Impedance plot of anode before discharge measured in H_2 flow.

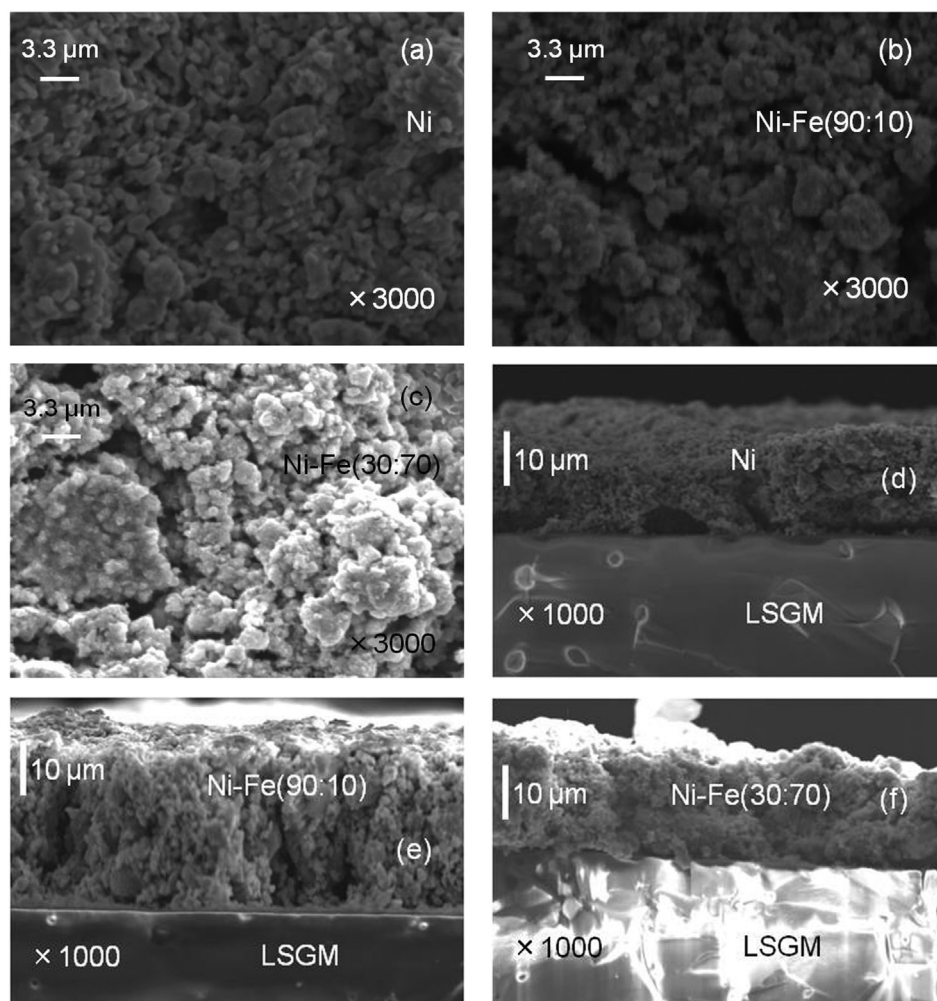


Fig. 2 – SEM images of (a)Ni, (b)Ni–Fe (90:10), (c)Ni–Fe (30:70), and cross sectional images of (d)Ni, (e)Ni–Fe (90:10), (f) Ni–Fe (30:70) before cell test.

Fe, we discuss the anode performance under higher H_2 concentration conditions, which is almost the same as the fuel cell condition. Fig. 1 shows the impedance plots of anode before discharge in H_2 -flow (3% H_2O in H_2 , 100 mL/min). The arc assigned to the polarization resistance was very different depending on the Fe content in the Ni–Fe anode. The smallest polarization resistance (1.1 ohm/cm^2) was observed with the electrode containing 10% of Fe in Ni–Fe. The pure Ni anode showed the largest polarization resistance (14.5 ohm/cm^2). Fe-rich Ni–Fe anode (Ni:Fe = 70:30, 50:50, 30:70) showed smaller polarization resistance compared with pure Ni anode. Therefore, the addition of Fe in small amounts into Ni enhances the activity of anode.

To consider the initial anode performance without redox cycling, initial state of anode should be discussed. Fig. 2(a), (b), and (c) shows the SEM images of anode calcined on the LSGM disk and reduced at 873 K for 1 h in humidified hydrogen. Particle size was similar in Ni, Ni–Fe (90:10), and Ni–Fe (30:70). Cross sectional images are shown in Fig. 2(d), (e) and (f). In the case of pure Ni anode and Ni–Fe (30:70) anode, poor contact between anode and LSGM electrolyte was observed in contrast

with very good contact between Ni–Fe (90:10) and LSGM. Additionally, it is clearly seen that Ni–Fe (90:10) anode has porous structure. It is unclear why only the Ni–Fe (90:10) anode has good contact and porous structure, but it would contribute to the cell performance. In actual, as already shown in Fig. 1, Ni–Fe(90:10) showed the lowest impedance.

Fig. 3 shows the first discharge curves of the Fe-air battery using Ni–Fe anodes containing different amount of Fe. The discharge potential of the cell with a pure Ni anode was very low and gradually decreased during discharge and no potential plateau was observed. Also in our previous report, when the operating temperature was high (973 K), discharge potential of the Fe-air battery was gradually decreased and no potential plateau was observed because of sintering of anode [11]. There are several possible reasons for this phenomenon. One explanation could be the degradation by sintering of the anode during discharge. Another reason may be a large concentration overpotential when decreasing the H_2 concentration, especially in the deep discharge state.

When Ni–Fe (90:10) was used as the anode, the highest discharge potential (1.026 V) was observed at 400 mAh/g of

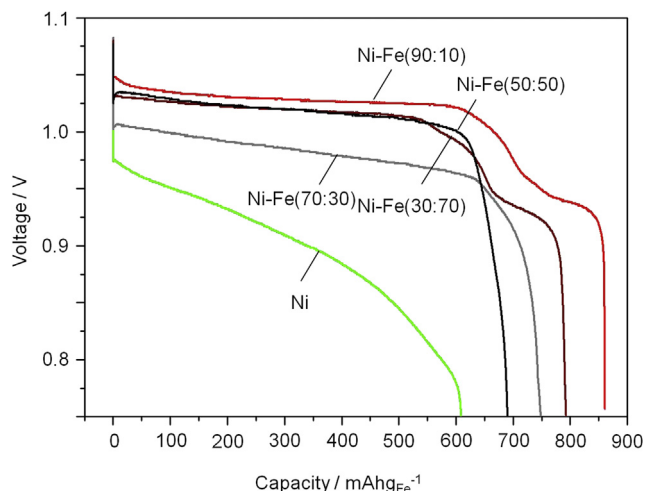


Fig. 3 – First discharge curves of the Fe-air cell using Ni-Fe anode containing different amount of Fe in Ni-Fe-based anode.

capacity. Other Fe-rich Ni-Fe anode cells, including Ni-Fe (70:30), Ni-Fe (50:50), and Ni-Fe (30:70) showed lower discharge potentials compared with the Ni-Fe (90:10) anode. This tendency is in good agreement with the polarization resistance estimated from AC impedance shown in Fig. 1. Therefore, smaller polarization resistance of the anode leads to the higher discharge potential.

In a rechargeable battery, both the first discharge performance and the cycle stability are important. Fig. 4(a) and (b) shows the discharge curves of the Fe-air batteries using Ni-Fe (90:10) as an anode for prolonged cycling, and the discharge potential of the Fe-air batteries using anodes with different amounts of Fe. In all of the cases, degradation by redox cycle was more serious than the case of cermet anode in our previous report since the combined oxide in anode can protect from the serious reoxidation [7]. However, in this report, it is important to understand the degradation character of metal, in particular, sintering behaviour. Ni-Fe (90:10) showed the highest discharge potential for all the cycle numbers. The cell using a pure Ni anode could not achieve a second discharge because of such severe degradation after the first discharge. The Ni-Fe anodes containing a large amount of Fe, such as Ni-Fe (30:70) also showed poor stability against redox cycling. Therefore, Ni-Fe (90:10) is the most suitable anode in terms of both its initial performance and its cycle stability.

Fig. 5(a), (b), and (c) shows the impedance plots of anode using Ni, Ni-Fe (90:10), and Ni-Fe (30:70), respectively. In the case of pure Ni, a significant degradation was observed after first discharge, particularly in terms of an increase in polarization resistance. In the case of Ni-Fe (90:10), this degradation was suppressed in comparison with the case of the pure Ni anode. It is reported that the Ni-Fe (90:10) electrode shows much higher stability against reoxidation compared with pure Ni in SOFCs using LaGaO₃ film electrolyte because iron is preferentially oxidized and protects Ni from further oxidation [17]. Therefore, in this study the Ni-Fe (90:10) anode is also protected from serious reoxidation because of the protective

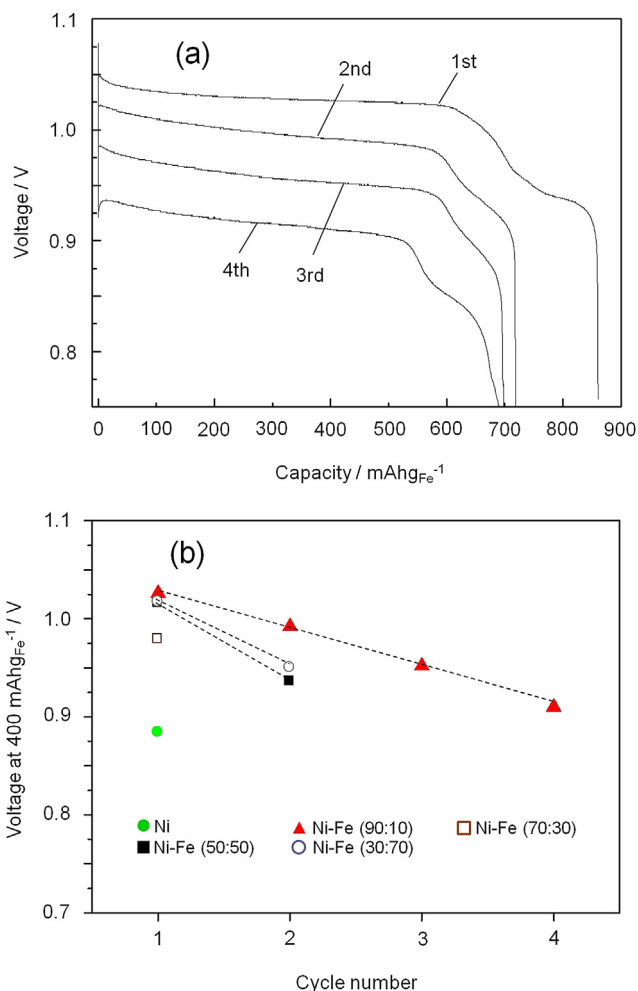


Fig. 4 – (a) Discharge curves of the cell using Ni-Fe (9:1) and (b) discharge potential of the various cells with different cycle number.

layer formed by the iron oxide. On the other hand, in the case of Ni-Fe (30:70) anode, serious degradation was observed after second discharge.

Fig. 6(a), (b) and (c) shows SEM images of tested Ni, Ni-Fe(90:10), and Ni-Fe(30:70), respectively. In the Pure Ni and Ni-Fe (30:70) anode, the aggregation of particles is more significant than that observed for the Ni-Fe (90:10) anode, even though the Ni-Fe (90:10) was cycled longer. As already mentioned, pure Ni is not protected from reoxidation with Fe, and therefore, it seems that serious aggregation was occurred. There are several possible reasons for the aggregation of the Fe-rich anode. Firstly, the Fe in the Fe-rich electrode might easily be separated from the Ni-Fe alloy and thus would not protect the Ni from reoxidation. A second reason could be that Fe might be preferentially reoxidized compared with Ni, in accordance with their theoretical oxidation potentials. Then, the larger amount of Fe in Ni-Fe anode would lead to a higher reoxidation of the anode during discharge. A further investigation of this phenomenon is currently under study in order to understand the mechanism for their different behaviours.

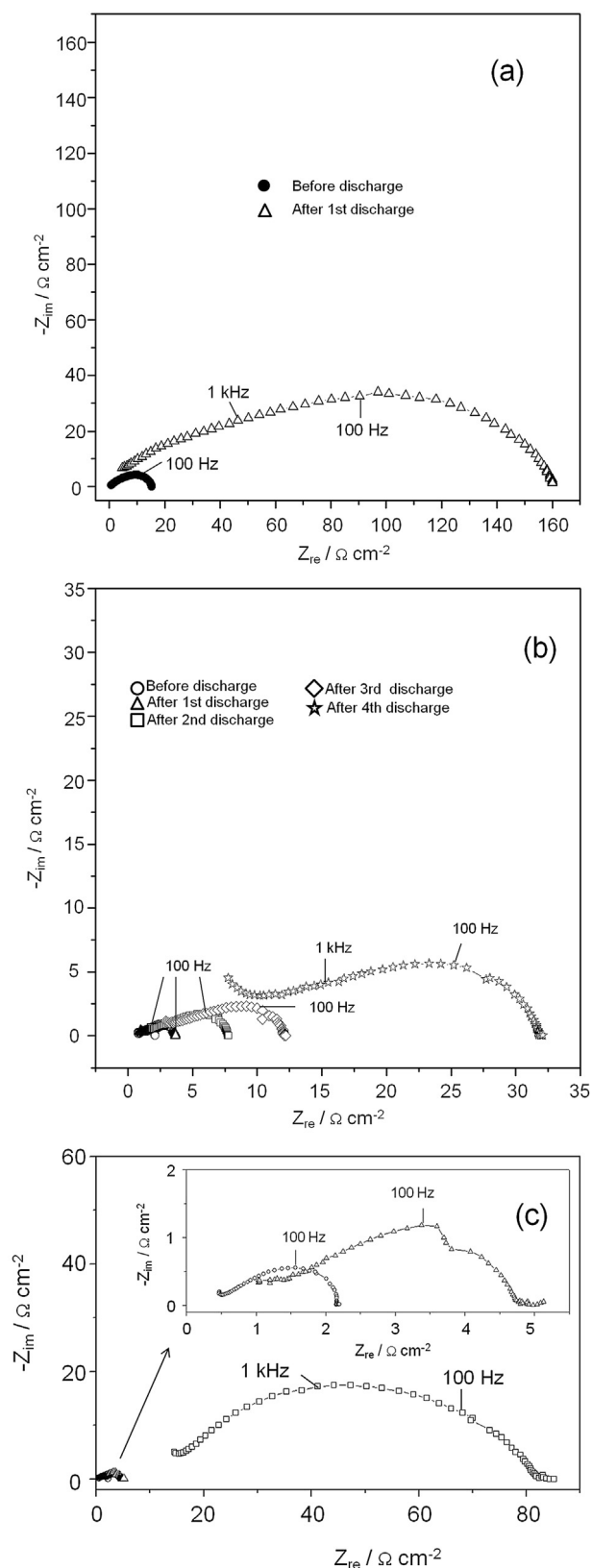


Fig. 5 – Impedance plots of anode using (a) Ni anode, (b) Ni–Fe (9:1) anode, and (c) Ni–Fe (3:7) anode.

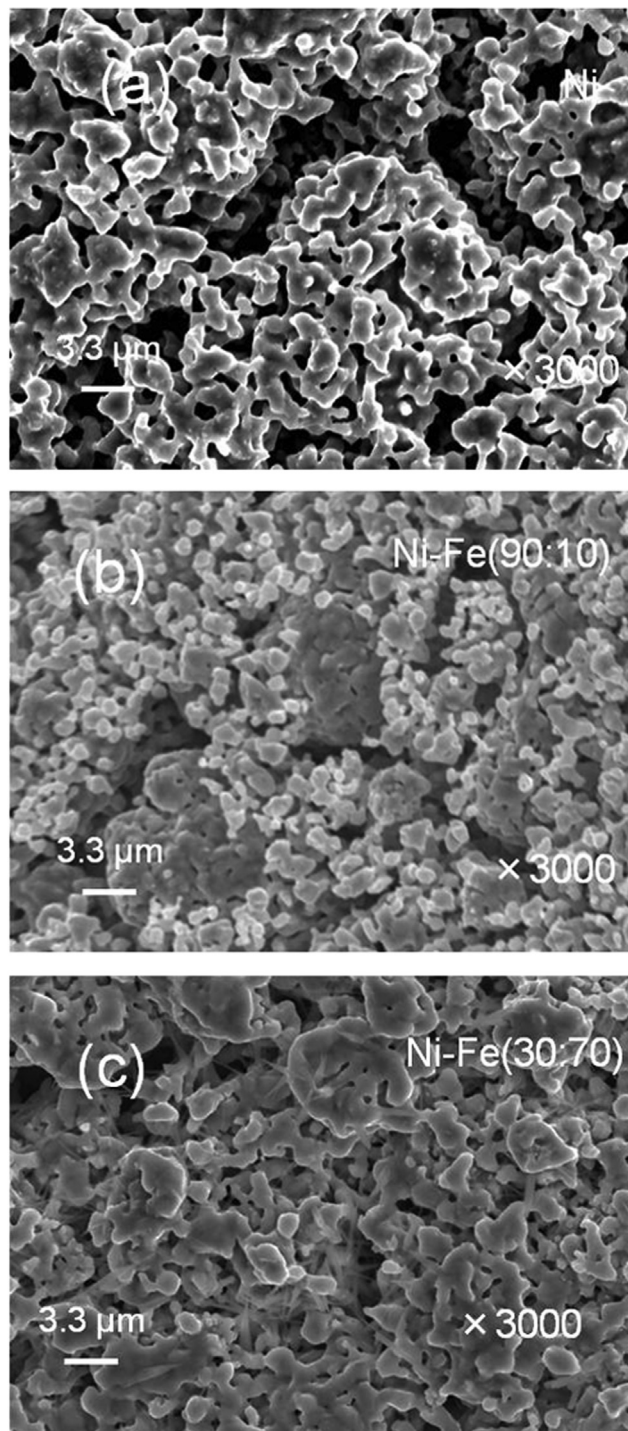


Fig. 6 – SEM images of anode after test. (a) Ni, (b) Ni–Fe (90:10), and (c) Ni–Fe (30:70).

Conclusion

The effect of the Ni/Fe ratio of the anode on the discharge performance and cycle stability for Fe-air rechargeable batteries using LaGaO₃-based oxide ion conducting electrolyte was studied. When a pure Ni anode was used, the lowest discharge potential and very low cycle stability was observed.

The addition of Fe to the anode is highly effective in terms of increasing the performance of the Fe-air battery. The highest stability and discharge potential were observed when the Ni–Fe (90:10) composition was used as the anode. Suppressed degradation of Ni–Fe (90:10) in comparison with pure Ni might be because of the protective layer formed by the iron oxide. A higher Fe content in the anode (e.g. Ni–Fe (30:70) ratio) decreases the cycle stability due to the aggregation of particles with increasing redox cycles.

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